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# PHOTOELECTROCHEMICAL BEHAVIOR OF CHLOROPHYLL a IN THIN FILMS

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## Abstract

The photoelectrochemical behavior of chlorophyll a species P740 (polymerized water adduct of chlorophyll a, absorbing at 740nm) was investigated using chlorophyll a thin films, electrodeposited on both $SnO_2$ and $SnO_2/TiO_2$ electrodes. The photocurrent action spectra of chlorophyll a in electrochemical devices are used to explain the chlorophyll a behavior in the process of charge generation under illumination and in the transfer of electrons. The use of nanoparticle-coated electrodes is promising for the building of efficient devices for light conversion, based on chlorophyll a.

## Keywords

Chlorophyll a, electron transfer, electronic structure, light activation, modeling, nanostructure, photoconversion, photoelectrochemistry

## 1. Introduction

Chlorophyll a is the major pigment in plant photosynthesis, being responsible for both light absorption and light induced charge separation. There has been much interest in photovoltaic and photoelectrochemical investigation of chlorophyll a and related pigments. Different types of photovoltaic devices have been studied; most of them using chlorophyll a in the form of solid layers coated on metal or semiconductor electrodes [1, 2]. In some photovoltaic experiments the chlorophyll a film sandwiched between two electrodes is sensitizing large bandgap semiconductors and extending their photoresponse in the visible domain [3, 4]. In photoelectrochemical measurements chlorophyll a was deposited on metal electrodes [5], but higher efficiencies for light photoconversion have been reported when chlorophyll was adsorbed on nanostructered semiconductor electrodes [6, 7]. As an extension of our previous work, done on photovoltaic devices with chlorophyll a [4, 8], we developed photoelectrochemical devices using chlorophyll a species absorbing at 740 nm. The experiments performed

on electrochemical devices using P740 chlorophyll a in thin films, electrodeposited on both $SnO_2$ and $SnO_2/TiO_2$ electrodes lead to a comparative study, and to the explanation of chlorophyll a behavior in the process of charge separation under illumination and of transfer of electrons.

## 2. Experimental section

### 2.1. MATERIALS

Chlorophyll a (Chla) was prepared from fresh spinach leaves by the Strain & Svec method and checked for purity (absorption and fluorescence in VIS). The chlorophyll a species P740 (polymerized water adduct of chlorophyll a, absorbing at 740nm) was obtained by dissolving the freshly prepared chlorophyll a in n-pentane (Merck), and maintaining the solution/suspension at temperatures below -10°C. Analytical grade solvents were used without further purification. The $SnO_2$ coated electrode was cut from a commercial transparent conducting glass plate, having the dimension 3x3cm$^2$ and sheet resistance 20 $\Omega$/sq. The optical transparency of the electrode was 85% in the visible wavelengths. The transparent conducting glass was chemically cleaned before use to remove any residual grease. The $SnO_2/TiO_2$ electrode was cut from a coated glass plate prepared at University of Uppsala. The Lindquist's procedure [9] for nanocrystalline $TiO_2$ film electrodes preparation yields films of 4 μm thickness, porous from the outer layer to the transparent conducting glass ($SnO_2$), with relatively uniform particle size of 15 nm in diameter [9]. The $SnO_2/TiO_2$ glass electrode (3x3cm$^2$) was heated for 10 min at 500°C, and then immersed in n-pentane. The chlorophyll a film was subsequently formed on the glass electrode.

### 2.2. FILM PREPARATION

Thin films of chlorophyll a were prepared by electrodeposition. On both types of electrodes, $SnO_2$ and $SnO_2/TiO_2$, a thin layer of chlorophyll a (of various thickness) was electrodeposited from the suspension/solution of chlorophyll a in n-pentane. The suspension/solution of chlorophyll a was sonicated before use, in order to get uniform size for suspended chlorophyll a molecular aggregates. The $SnO_2$ or $SnO_2/TiO_2$ coated glass electrode was the cathode, and the applied electric field had an intensity of 1000V/cm. The film thickness was controlled by varying the molar concentration of Chla solution and/or by varying the electrodeposition time. The film thickness was estimated from the absorption spectra, using the O.D. at 740 nm. The optical absorption spectra of the films were obtained on a double beam UV - VIS spectrophotometer Lambda 2S Perkin Elmer & PECSS software.

### 2.3. PHOTOELECTROCHEMICAL MEASUREMENTS

The $SnO_2$ and $SnO_2/TiO_2$ electrodes coated with a thin film of P740 chlorophyll a represented the working electrode in a three-electrode electrochemical cell. A Pt foil was used as the counter electrode and a standard Ag/AgCl (saturated KCl in water) electrode as the reference. Solutions of $Na_2SO_4$ of different ionic strengths in phosphate

buffers (pH range: 6.9 - 8) were used as electrolytes. μAUTOLAB (Eco-Chemie) electrochemical analyzer and GPES software were used to perform the experiments on the electrochemical cell. The working electrode (on area of about 0.4 cm$^2$) was illuminated by monochromatic light (in the spectral range 350 - 800 nm) using a halogen lamp of 650 W. The amperometric mode was used and the photocurrents represented the difference between the currents under illumination (different wavelengths) and dark currents. All measurements were performed in air and at room temperature. Photocurrent action spectra were obtained by plotting the photocurrents, measured for a given electrode voltage at different wavelengths. The action spectra were corrected to equal photon density at each wavelengths and normalized (the peak at 800 nm is unity).

## 3. Results and discussions

### 3.1. PHOTOELECTROCHEMICAL STUDIES

The spectral behavior of the photoelectrochemical cells was investigated and compared with the absorption spectrum of chlorophyll a films. Anodic photocurrents have been observed at both $SnO_2$ and $SnO_2/TiO_2$ electrodes with electrodeposited chlorophyll a film under potential-controlled conditions, in the range more anodic than –0.17 V vs. Ag/AgCl. Typical photocurrent spectra are illustrated in Figures 1 and 2 together with the corresponding absorption spectra of chlorophyll a films.
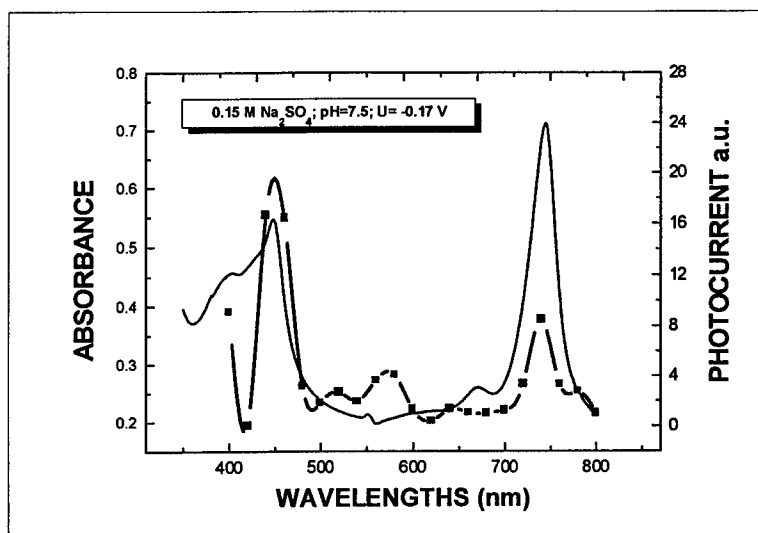


*Figure 1.* Photocurrent spectrum of Chl a on $SnO_2/TiO_2$ electrode (dotted line) and absorption spectrum of the chlorophyll a film

As is evident from Figure 1, the action and absorption spectra coincide fairly well when chlorophyll a was electrodeposited on the $SnO_2/TiO_2$ electrode. This means that chlorophyll a is sensitizing the $SnO_2/TiO_2$ composite system. The absorption spectrum of the chlorophyll a film shows the Soret band and the red ($Q_y$) band shifts to 740 nm. This indicates that the polymerized water adduct of chlorophyll a, absorbing at 740 nm, determines the photoresponse of the composite system. This special molecular aggregate of chlorophyll a is known as "microcrystalline chlorophyll a" [10] or as "micelle chlorophyll a"[11]. The size of these molecular aggregates (P740), either crystalline or micelle, having a specific absorption at 740 nm, is in the range of tens to hundred of nm. The chlorophyll a film thickness was in the range of 100 nm, as estimated from optical density at 740 nm.
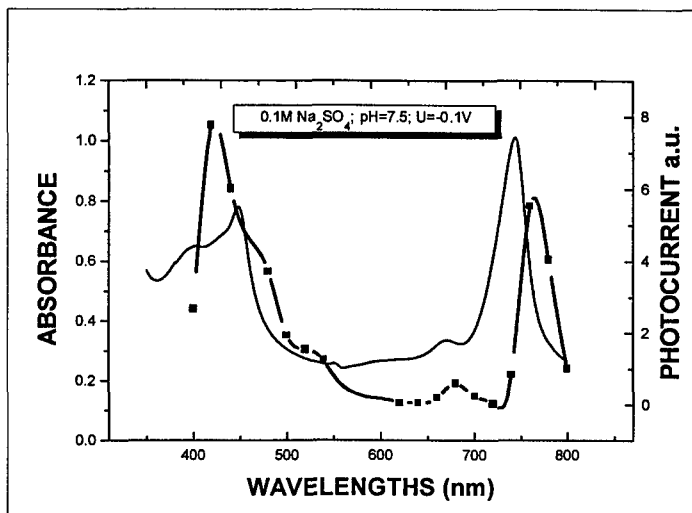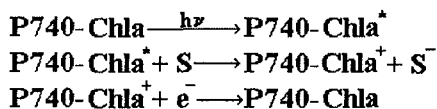


*Figure 2*. Photocurrent spectrum of Chl a on $SnO_2$ electrode (dotted line) and absorption spectrum of the chlorophyll a film

The same chlorophyll a species, as resulting from the absorption spectrum presented in Figure 2, but electrodeposited on $SnO_2$ electrode, is responsible for the photoeffects represented by the action spectrum in the same figure. The red band in the action spectrum presents a small shift of about 20 nm, as compared with the $Q_y$ band of chlorophyll a film absorption. All investigated photoelectrochemical cells, prepared by electrodeposition of chlorophyll a on $SnO_2$ electrodes, presented the same type of behavior, regardless of chlorophyll a film thickness or electrolyte characteristics.

Generation of anodic photocurrents was interpreted schematically in terms of the electron donation from excited P740-chlorophyll a to $SnO_2$ or $SnO_2/TiO_2$ electrode, followed by the reduction of Chl a cation by the free electrons from the electrolyte solution:

$$P740\text{-}Chla \xrightarrow{\ h\nu\ } P740\text{-}Chla^{*}$$
$$P740\text{-}Chla^{*} + S \longrightarrow P740\text{-}Chla^{+} + S^{-}$$
$$P740\text{-}Chla^{+} + e^{-} \longrightarrow P740\text{-}Chla$$

S being the semiconductor electrode (SnO$_2$ or SnO$_2$/TiO$_2$) of the electrochemical cell.

The energy diagram (Figure 3) depicts the band energies of electrodes and oxidation potential of chlorophyll a. In both cases, the more negative value of the excited state of chlorophyll a facilitates the photoinduced electron transfer from chlorophyll a to the semiconductor electrode. In case A, there is a close interaction between the large molecular aggregates of P740 chlorophyll a and the polar surface of SnO$_2$. As a consequence, the electric field at the interface chlorophyll a/SnO$_2$ electrode affects the energy levels of the photoactive P740-chlorophyll a. This explains the difference between photocurrent action spectrum and film absorption in the case of photoelectrochemical cells with P740-chlorophyll a electrodeposited on SnO$_2$ electrodes.
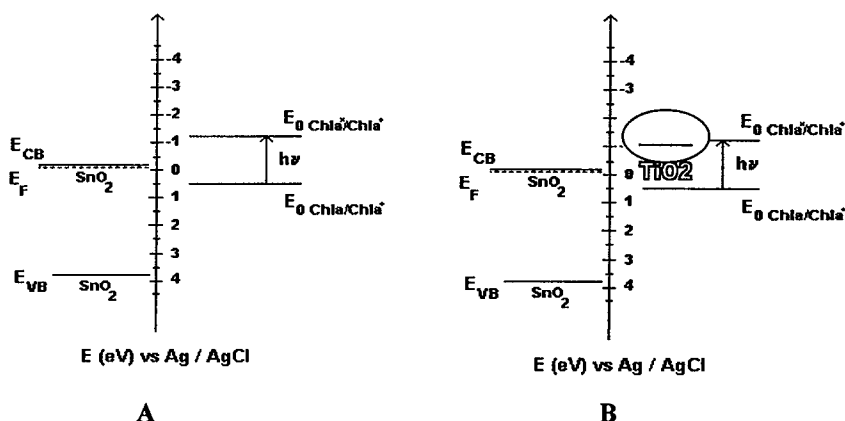


*Figure 3.* Schematic energy diagrams at the interface:
chlorophyll a/SnO$_2$electrode (A),chlorophyll a/SnO$_2$/TiO$_2$electrode (B)

In case B, the electrolyte ions permeate the nanocrystalline TiO$_2$ film and, as in normal solution electrochemistry, the mobile ions neutralize any electric field. At normal concentrations (0.1- 0.5 M), the electrolyte prevents the extension of an electric field of over more than 20-50 nm [12]. As a consequence, a coincidence between the action spectrum and the absorption spectrum of P740 chlorophyll a is expected. This coincidence is illustrated in Figure 1. This also means that in the case of nanostructured electrode SnO$_2$/TiO$_2$, the photoinduced electron transfer from chlorophyll a to electrode is not field-assisted. Under illumination chlorophyll a, excited to a higher electronic state, injects electrons into TiO$_2$ particles. These electrons are then collected at the interface SnO$_2$/TiO$_2$ to produce anodic photocurrents.

A further conclusion is that the large chlorophyll a molecular aggregates, electrodeposited on porous film of TiO$_2$ nanoparticles, are closer outside the ionic double layer at the solid/solution interface. This is also supported by the observed dependence of the electrochemical cell photoresponse on the pH value of the electrolyte solution.

Figure 4 presents the pH dependence of the photoresponse when using electrochemical cells with the same thickness of chlorophyll a film, and electrolyte solutions with the same ionic strength. The value of 7.5 was found to be the optimum pH. Chlorophyll a loses the central Mg through chemical reaction with protons; at acidic pH, chlorophyll undergoes a decomposition resulting in the formation of pheophytin a. This known instability of chlorophyll a species could be the explanation for the observed behavior of photoresponse in electrochemical cells using more acidic electrolytes.
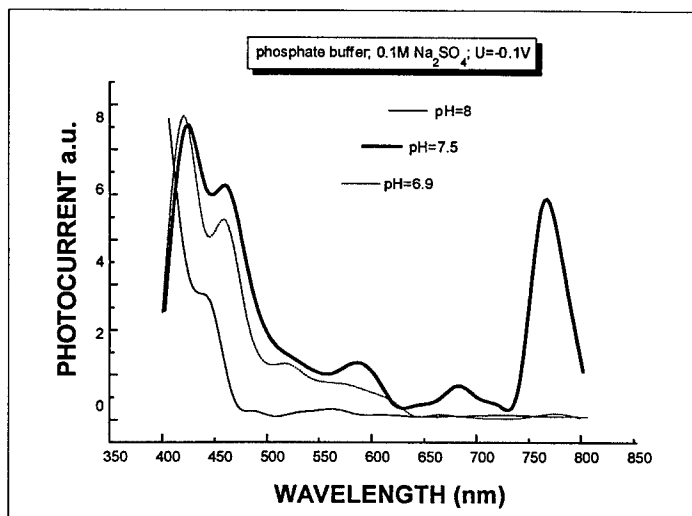


*Figure 4.* Photocurrent spectra of Chl a on $SnO_2/TiO_2$ electrode
at different pH values of the electrolyte

A change in the pH of the electrolyte solution causes, in many situations, a shift of the semiconductor electrode potential, induced by the dissociation equilibrium of protons at the electrode surface [13]. In the studied electrochemical cells, the electrode potential can exhibit cathodic shift by increasing pH. A shift of the electrode potential to more negative values affects the driving force for the photoinduced electron transfer from chlorophyll a to the electrode. The energy difference between the excited dye and the semiconductor is critical in controlling the electron transfer. This explains the situation illustrated in Figure 4: a photoresponse is only present when illuminating with the wavelengths corresponding to the Soret band of chlorophyll a absorption spectrum, i.e. exciting chlorophyll species to the second (higher) singlet state.

## 3.2. EFFICIENCY OF PHOTOCURRENT GENERATION

As already shown, P740 chlorophyll a manifests the ability to sensitize large bandgap semiconductors like $SnO_2$ and $TiO_2$. The electron transfer is taking place from the excited state of chlorophyll a to the semiconductor. Photoelectrochemical solar cells based on chlorophyll a could be easily obtained. The incident photon to current

conversion efficiency (IPCE), is obtained from the measurements of short circuit photocurrents at various wavelengths and using the following equation [14]:

$$IPCE(\%) = \frac{Isc}{Iinc} \frac{1240}{\lambda} 100$$

where *Isc* is the short circuit photocurrent, $\lambda$ is the wavelength and *Iinc* is the light intensity incident on chlorophyll a. A maximum IPCE of 1.2%, at 740 nm incident light, was obtained for the photoelectrochemical cell, with photocurrent action spectrum presented in Figure 5. The chlorophyll a film thickness is less than 100nm. Making the corrections for absorption, a value of about 2% can be considered.
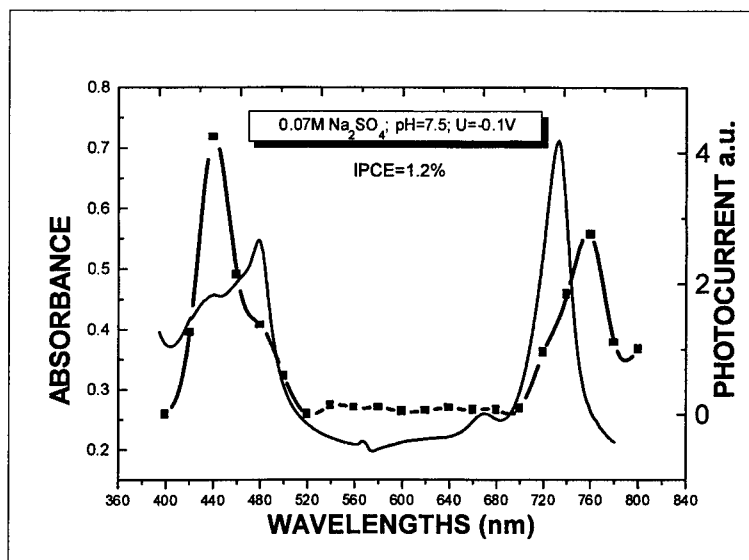


*Figure 5.* Photocurrent spectrum of Chl a on SnO₂ electrode (dotted line) and absorption spectrum of the chlorophyll a film

Optimization of the photoelectrochemical cell, with respect to the efficient charge photogeneration and reduction of recombination losses, can be achieved by controlling the parameters of both chlorophyll a sensitized electrode and electrolyte solution.

## 4. Conclusion

The present study of photoelectrochemical devices based on P740 chlorophyll a, electrodeposited as thin films on large band gap semiconductors, leads to the conclusion that chlorophyll a is the photoactive component. The nature of the semiconductor electrode (i.e. nanoparticulate, porous or uniform film) at the interface with P740 chlorophyll a thin film proved to be the dominant factor in controlling the photoinduced electron transfer.

## Acknowledgments

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